# CAPACITOR OF SEMICONDUCTOR MEMORY DEVICE THAT HAS COMPOSITE Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> DIELECTRIC LAYER AND METHOD OF MANUFACTURING THE SAME

## **BACKGROUND OF THE INVENTION**

This application claims priority from Korean Patent Application No. 2002-69997, filed on November 12, 2002, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference. Also, this application is a Continuation-In-Part (C.I.P.) of application Ser. No. 10/452,97, filed on June 2, 2003.

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#### 1. Field of the Invention

The present invention relates generally to integrated circuits and a method of manufacturing the same, and more particularly, to a semiconductor device that has a dielectric structure capable of enhancing electrical characteristics, and a method of manufacturing the same.

# 2. Description of the Related Art

The increasing integration density of semiconductor devices needs a capacitor of a DRAM having greater capacitance per unit area. To meet this requirement, a variety of methods have been introduced. Such methods include a method of increasing the electrode surface area of the capacitor by forming a three-dimensional stacked, cylindrical, or trench type electrode or by forming hemispherical grains on the electrode surface, a method of thinning a dielectric layer, a method of forming the dielectric layer using of high-dielectric material having a high dielectric constant or a ferroelectric material and so on. However, the above methods are not without their limitations. For example, reducing the thickness of the dielectric layer seriously increases leakage current as the capacitance increases. When a material having a high dielectric constant, for example, Ta<sub>2</sub>O<sub>5</sub> or BST((Ba,Sr)TiO<sub>3</sub>), is used for the dielectric layer, polysilicon, which has been conventionally used to form the electrode, cannot be used. This is because the use of the polysilicon causes tunneling and increases leakage current when the thickness of the dielectric layer is reduced.

As another method for increasing capacitance per unit area of the capacitor, a metal-insulator-metal (MIM) capacitor whose electrode is formed of, instead of polysilicon, a metal having a large work function, such as TiN or Pt, has been suggested. In this method, the growth of a native oxide layer on the metal electrode is suppressed to prevent a capacitance

Docket No. 9898-321 Client No. SS-18146-US reduction by a low-dielectric oxide layer. In the MIM capacitor, an oxide of a metal having a great affinity for oxygen is mostly used for a dielectric layer.

Recently, in order to resolve problems caused by increase in leakage current with reduced thickness of the dielectric layer, forming a composite dielectric layer, which includes a conventional dielectric layer and a higher dielectric constant layer, instead of a single dielectric layer, has been suggested. The formation of the composite dielectric layer prevents leakage current from increasing due to the use of the higher dielectric constant layer, without reducing capacitance, and improves the electrical properties of the capacitor.

a needs still exists for Particularly, a great deal of research has been conducted into a dual or multi-dielectric layer including a Al<sub>2</sub>O<sub>3</sub> layer, which has a small dielectric constant of about 10 but effectively prevents leakage current, and an HfO<sub>2</sub> layer, which has a large dielectric constant of 20-25 and effectively prevents leakage current due to its large band gap.

### SUMMARY OF THE INVENTION

The present invention provides a capacitor of a highly integrated semiconductor memory device that includes a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer with a layer thickness ratio that is optimized for maximum suppression of leakage current.

The present invention also provides a method of manufacturing a capacitor of a semiconductor memory device that includes a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer with a layer thickness ratio that is optimized for maximum suppression of leakage current. According to an aspect of the present invention, there is provided capacitor of a semiconductor memory device, the capacitor comprising: a lower electrode; a composite dielectric layer including an Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer sequentially formed on the lower electrode, the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a thickness greater than or equal to the HfO<sub>2</sub> dielectric layer; and an upper electrode formed on the composite dielectric layer.

According to specific embodiments of the capacitor, the Al<sub>2</sub>O<sub>3</sub> dielectric layer may have a thickness of 30-60Å. The HfO<sub>2</sub> dielectric layer may have a thickness of 40Å or less, for example, 10-40Å. The lower electrode is made of one of polysilicon, metal nitride, and noble metal. Preferably, the lower electrode is made of one selected from the group consisting of TiN, TaN, WN, Ru, Ir, Pt, and a composite layer of the forgoing materials. When the lower electrode is made of polysilicon, the capacitor according to the present invention may further includes a silicon nitride layer between the lower electrode and the composite dielectric layer.

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The upper electrode may be made of one of polysilicon, metal nitride, and noble metal. Preferably, the upper electrode is made of one selected from the group consisting of TiN, TaN, WN, Ru, Ir, Pt, and a composite layer of the forgoing materials.

An alternative capacitor according to the present invention includes: a lower electrode made of one of metal nitride and noble metal; an upper electrode made of one of metal nitride and noble metal; a composite dielectric layer, formed between the lower electrode and the upper electrode, that includes an Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer with a thickness ratio of Al<sub>2</sub>O<sub>3</sub> to HfO<sub>2</sub> that is greater than or equal to 1.

According to another aspect of the present invention, there is provided a method of manufacturing a capacitor of a semiconductor memory device, the method including forming a lower electrode on a semiconductor substrate. Next, a composite dielectric layer is formed on the lower electrode, wherein the composite dielectric layer includes an Al<sub>2</sub>O<sub>3</sub> dielectric layer having a first thickness and an HfO<sub>2</sub> dielectric layer having a second thickness, the second thickness being smaller than or equal to the first thickness. An upper electrode is formed on the composite dielectric layer.

According to specific embodiments of the capacitor manufacturing method, each of the Al<sub>2</sub>O<sub>3</sub> dielectric layer and the HfO<sub>2</sub> dielectric layer may be formed using one of chemical vapor deposition and atomic layer deposition. The method may further include thermally treating the composite dielectric layer. In which case, thermally treating the composite dielectric layer is performed in a vacuum, in an oxygen atmosphere, in an inert gas atmosphere by rapid thermal annealing, by furnace annealing, plasma annealing, or UV annealing.

Since a capacitor of a semiconductor memory device according to the present invention has a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer with a thickness ratio of Al<sub>2</sub>O<sub>3</sub> to HfO<sub>2</sub> that is greater than or equal to 1, the leakage current characteristics of the capacitor are improved. With the capacitor according to the present invention that includes the composite

Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer with optimal thickness ratio between the two dielectric layers, the effect of suppressing increase in leakage current is maximized and superior electrical properties are obtained.

# BRIEF DESCRIPTION OF THE DRAWINGS

The above objects and advantages of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings in which:

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- FIGS. 1A through 1E are sectional views illustrating step by step a method of manufacturing a capacitor of a semiconductor memory device according to an embodiment of the present invention;
- FIG. 2 is a graph of current leakage distribution versus equivalent oxide thickness (Toxeq) for various composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layers having different thickness ratios of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer;
  - FIG. 3 is a table of leakage current characteristics for capacitors with various composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layers having different thickness ratios of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer;
  - FIG. 4 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a constant thickness, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer;
  - FIG. 5 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a constant thickness, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer;
  - FIG. 6 is a graph of leakage current characteristics of capacitors having a single Al<sub>2</sub>O<sub>3</sub> dielectric layer, which was measured for comparison;
  - FIG. 7 is a graph of measured leakage current versus thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer, which are manufactured by the method according to the present invention and whose HfO<sub>2</sub> dielectric layer has a constant thickness;
  - FIG. 8 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a constant thickness, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer manufactured by the method according to the present invention;
  - FIG. 9 shows atomic force microscopic (AFM) images with respect to thickness of the HfO<sub>2</sub> layer;
  - FIG. 10 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a constant thickness, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer manufactured by the method according to the present invention;
  - FIGS. 11 and 12 are graphs of measured leakage current for different capacitors with a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer when a thickness ratio of Al<sub>2</sub>O<sub>3</sub> to HfO<sub>2</sub> is smaller than 1; and

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FIGS. 13 and 14 are graphs of measured leakage current for different capacitors with a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer when a thickness ratio of Al<sub>2</sub>O<sub>3</sub> to HfO<sub>2</sub> is greater than or equal to 1 according to the present invention.

## **DETAILED DESCRIPTION OF THE INVENTION**

Exemplary embodiments of the present invention described below may be varied in many different forms, and the scope of the present invention is not limited to the following embodiments; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity.

FIGS. 1A through 1D are sectional views illustrating step-by-step a method of manufacturing a capacitor of a semiconductor memory device according to an embodiment of the present invention. Referring to FIG. 1A, a lower electrode 120 is formed on a semiconductor substrate 110 to a thickness of tens to hundreds of angstroms. The lower electrode 120 may be formed of polysilicon, a metal nitride, or a noble metal. For example, the lower electrode 120 may be formed of a single layer of doped polysilicon, TiN, TaN, WN, Ru, Ir, or Pt, or a composite layer of these materials. When the lower electrode 120 is formed of doped polysilicon, a silicon nitride layer (not shown) is formed on the surface of the lower electrode 120 through rapid thermal nitridation (RTN) so as to prevent the lower electrode 20 from being oxidized during a subsequent thermal process.

Referring to FIG. 1B, a Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 is formed on the lower electrode 120 to a thickness of about 20-60Å, preferably, about 30-60Å. The Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 is formed to be thicker than or of equal thickness to an HfO<sub>2</sub> dielectric layer 134 (refer to FIG. 1C). The reason for this will be described later.

The Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 may be formed using chemical vapor deposition (CVD) or atomic layer deposition (ALD). When the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 is formed using ALD, sequential deposition processes are carried out with trimethylaluminum (TMA) as a first reactant and O<sub>3</sub> as a second reactant, at a temperature of 200-500°C and a pressure of 0.1-5 torr. The deposition and purging processes are repeated until the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 having a desired thickness is obtained. In addition to TMA, other examples of a first reactant for forming the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 include AlCl<sub>3</sub>, AlH<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>15</sub>AlO, (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>AlH, (CH<sub>3</sub>)<sub>2</sub>AlCl, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al, (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>Al, and the like. Other examples of a second reactant for forming the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 include activated oxidizing

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agents, such as  $H_2O$ ,  $H_2O_2$ , plasma  $N_2O$ , plasma  $O_2$ , and the like. When the  $Al_2O_3$  dielectric layer 132 is formed using  $O_3$  as the second reactant, the Al2O3 dielectric layer 132 has a similar dielectric constant and leakage current characteristics but is more reliable, compared to the case of using  $H_2O$  as the second reactant.

Referring to FIG. 1C, an HfO<sub>2</sub> dielectric layer 134 is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132. As a result, a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer is formed. The HfO<sub>2</sub> dielectric layer 134 has a thickness greater than or equal to the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132. The HfO<sub>2</sub> dielectric layer 134 has, preferably, a thickness of 40 Å or less, more preferably, 10-40Å.

The HfO<sub>2</sub> dielectric layer 134 may be formed using CVD or ALD. When the HfO<sub>2</sub> dielectric layer 134 is formed using CVD, deposition is carried out with an Hf source material and O<sub>2</sub> gas at a temperature of about 400-500°C and a pressure of about 1-5 torr. Examples of the Hf source material include HfCl<sub>4</sub>, Hf(OtBu)<sub>4</sub>, Hf(NEtMe)<sub>4</sub>, Hf(MMP)<sub>4</sub>, Hf(NEt<sub>2</sub>)<sub>4</sub>, Hf(NMe<sub>2</sub>)<sub>4</sub>, and the like.

When the HfO<sub>2</sub> dielectric layer 134 is formed using ALD, deposition is carried out with a metal organic precursor as an Hf source and H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, alcohols containing an –OH radical, or O<sub>3</sub> or O<sub>2</sub> plasma, as an oxygen source, at a temperature of about 150-500°C and a pressure of about 0.1-5 torr. Examples of the Hf source include HfCl<sub>4</sub> and metal organic precursors, such as Hf(OtBu)<sub>4</sub>, Hf(NEtMe)<sub>4</sub>, Hf(MMP)<sub>4</sub>, Hf(NEt<sub>2</sub>)<sub>4</sub>, and Hf(NMe<sub>2</sub>)<sub>4</sub>. The deposition and purging processes are repeated until the HfO<sub>2</sub> dielectric layer 134 having a desired thickness is obtained. When ALD is applied to form the HfO<sub>2</sub> dielectric layer 134, low-temperature deposition, effective step coverage, and easy thickness control are ensured. The HfO<sub>2</sub> dielectric layer 134 manufactured through either of the above-described methods has good leakage current characteristics and high reliability.

Referring to FIG. 1D, the HfO<sub>2</sub> dielectric layer 134 is thermally treated, as indicated by reference numeral 136. This thermal treatment 136 is performed to perfect stochiometry which is imperfect due to insufficient oxygen when the layer is grown rapidly for mass production, to repair defects occurring during the deposition, and to transition to crystalline state for a high dielectric constant. Further, through the thermal treatment 136, impurities can be removed from the HfO<sub>2</sub> dielectric layer 134, and the density of the HfO<sub>2</sub> dielectric layer 134 can be increased. The thermal treatment 136 may also have a curing effect.

Examples of the thermal treatment 136 includes thermal treatment in a vacuum, thermal treatment in an oxygen atmosphere, rapid thermal annealing in an oxygen or inert gas

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atmosphere, furnace annealing, plasma annealing, UV annealing, and the like. Examples of oxygen gas for RTA include  $O_2$ ,  $N_2O$ , and the like, and examples of inert gas for RTA include  $N_2$ , Ar, and the like. The thermal treatment 136 may be followed by additional thermal treatment in an  $O_3$  or  $O_2$  plasma atmosphere if required. Alternatively, additional thermal treatment may be performed before the thermal treatment 136. Both the thermal treatment 136 and additional treatment may be omitted if required.

Referring to FIG. 1E, an upper electrode 140 is formed on the HfO<sub>2</sub> dielectric layer 134 to a thickness of about 50-2000Å. The upper electrode 140 is formed of a single layer of polysilicon, a metal nitride, or a noble metal, or a composite layer of these materials. For example, the upper layer 140 may be formed of a single layer of polysilicon, TiN, TaN, WN, Ru, Ir, or Pt, or a composite layer of these materials. Suitable examples of composite layers for the upper electrode 40 include a TiN/polysilicon layer, a TaN/polysilicon layer, a Ru/TiN layer, and the like. The upper electrode 140 may be formed using ALD, CVD, or metalorganic chemical vapor deposition (MOCVD), with MOCVD being more preferred. When the upper electrode 140 is formed using MOCVD, a metal organic material, which contains no Cl atom that is a kind of contamination source, is used as a source metal material.

As described above, a capacitor according to the present invention includes a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer composed of the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 and the HfO<sub>2</sub> dielectric layer 134, which has the same or smaller thickness than the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132. In other words, a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 to the HfO<sub>2</sub> dielectric layer 134 is greater than or equal to 1. The leakage current characteristics of the capacitor are improved by such a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer structure. By forming the thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer 132 in a range of 30-60Å, direct tunnelling through the dielectric layer of the capacitor is suppressed and the composite dielectric layer has stable current leakage current characteristics.

FIG. 2 is a graph of current leakage distribution versus equivalent oxide thickness (Toxeq) for various composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layers having different thickness ratios of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer. In FIG. 2, as is apparent from the circles designated by A1 and A2, leakage current characteristics are deteriorated for composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layers whose Al<sub>2</sub>O<sub>3</sub> dielectric layer is thicker than their HfO<sub>2</sub> dielectric layer. Dashed lines designated by B indicate a normal current distribution.

FIG. 3 is a table of leakage current characteristics for capacitors with various composite  $Al_2O_3/HfO_2$  dielectric layers having different thickness ratios of the  $Al_2O_3$  dielectric layer to the  $HfO_2$  dielectric layer. The figures in FIG. 3 indicate the equivalent

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oxide thickness of each of the sample capacitors. As is apparent from FIG. 3, leakage current deterioration is more serious for capacitors with smaller thickness ratios of the  $Al_2O_3$  dielectric layer to the  $HfO_2$  dielectric layer.

FIG. 4 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a thickness of 20Å, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer. In FIG. 4, "T<sub>ox</sub>" denotes equivalent oxide thickness.

As is apparent from FIG. 4, when a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is less than 1.0, i.e., when the thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer is smaller than the thickness of HfO<sub>2</sub> dielectric layer, leakage current characteristics are deteriorated. When a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is equal to 1.0, i.e., when the Al<sub>2</sub>O<sub>3</sub> dielectric layer and the HfO<sub>2</sub> dielectric layer have the same thickness, leakage current characteristics are favorable.

FIG. 5 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a thickness of 35Å, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer. In FIG. 5, when a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is less than 1.0, the leakage current characteristics are deteriorated. When a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is greater than 1.0, the leakage current characteristics are favorable.

FIG. 6 is a graph of leakage current characteristics of capacitors having a single  $Al_2O_3$  dielectric layer, which was measured for comparison. As shown in FIG. 6, as the thickness of the  $Al_2O_3$  dielectric layer becomes smaller, the equivalent oxide thickness (Tox) is reduced. The leakage current of the  $Al_2O_3$  dielectric layer is abruptly increased at a thickness of 33Å. From the results of FIG. 6, it is apparent that reducing the thickness of the single  $Al_2O_3$  dielectric layer is limited at an equivalent oxide thickness of about 30Å, in consideration of the leakage current characteristics of the  $Al_2O_3$  layer.

FIG. 7 is a graph of measured leakage current versus thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer, which is manufactured by the method according to the present invention and whose HfO<sub>2</sub> dielectric layer has a thickness of 20Å. In FIG. 7, when the Al<sub>2</sub>O<sub>3</sub> dielectric layer has a thickness of 20Å and 25Å, the leakage current is greatly increased at a low voltage of 2V or less. When the Al<sub>2</sub>O<sub>3</sub> dielectric layer has a thickness of 30Å and 35Å, almost the same leakage current

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characteristics as when a single Al<sub>2</sub>O<sub>3</sub> dielectric layer is used appear, despite a small equivalent oxide thickness of the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer.

FIG. 8 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a thickness of 30Å, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer manufactured by the method according to the present invention.

In FIG. 8, as the thickness of the HfO<sub>2</sub> dielectric layer is increased, the leakage current is reduced. Although a degree of improvement in leakage current characteristics is small compared to increasing the thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer, as is apparent from FIG. 8, the effect of increasing the thickness of the HfO<sub>2</sub> dielectric layer on the equivalent oxide thickness is minor.

As described above, in a capacitor with such a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer, leakage current characteristics are more dependent on the thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric layer than on the thickness of the HfO<sub>2</sub> dielectric layer. Therefore, to attain stable leakage current characteristics in capacitors with the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer, it is preferable that the thickness of the Al<sub>2</sub>O<sub>3</sub> dielectric is 30Å or greater.

In general, as the deposition thickness of the HfO<sub>2</sub> layer increases, more crystallization occurs during the deposition. This effect can be identified using an atomic force microscope (AFM).

FIG. 9 shows AFM images with respect to thickness of the HfO<sub>2</sub> layer. As shown in FIG. 9, when the HfO<sub>2</sub> layer has a thickness of 60Å, surface roughness is greatly increased. When the thickness of the HfO<sub>2</sub> layer is increased, partial crystallization occurs within the HfO<sub>2</sub> layer. Also, the crystallized portion of the HfO<sub>2</sub> layer grows more rapidly than an amorphous portion. As is apparent from the AFM images of FIG. 9, when the HfO<sub>2</sub> layer has a thickness of 60Å, the HfO<sub>2</sub> layer grows in a needle shape and has rougher surface.

According to the result of an AFM analysis, the HfO<sub>2</sub> layer starts to crystallize at a thickness of about 50Å.

FIG. 10 is a graph of measured leakage current versus thickness of the HfO<sub>2</sub> dielectric layer, which is formed on the Al<sub>2</sub>O<sub>3</sub> dielectric layer having a thickness of 25Å, for different capacitors having the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer manufactured by the method according to the present invention.

Contrary to the expectation that the thicker HfO<sub>2</sub> dielectric layer is, the more the high dielectric layer will improve leakage current characteristics, which is a known advantage of the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer structure, in FIG. 10, the leakage current

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characteristics are deteriorated when the thickness of the HfO<sub>2</sub> dielectric layer is increased. This result is believed to be related with the crystallization of the HfO<sub>2</sub> dielectric layer. In other words, as the thickness of the HfO<sub>2</sub> dielectric layer is increased, crystalline HfO<sub>2</sub> grains grow. The HfO<sub>2</sub> grains grown into the Al<sub>2</sub>O<sub>3</sub> layer of the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer structure serve as leakage current paths within the dielectric layer and deteriorate the leakage current characteristic.

As is apparent from the above measurement results, in order to maximize the effect of the HfO<sub>2</sub> layer reducing the leakage current in capacitors with such a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer structure, it is preferable that the thickness of the HfO<sub>2</sub> dielectric layer is determined to be smaller than the thickness at which crystallization of the HfO<sub>2</sub> layer is initiated, for example, to be about 40Å or less based on the results of the AFM analysis.

FIGS. 11 and 12 are graphs of measured leakage current versus thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer, when the thickness ratio is smaller than 1, for different capacitors with the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer. In FIGS. 11 and 12, the leakage current characteristic of a capacitor with a single Al<sub>2</sub>O<sub>3</sub> dielectric layer is also shown for comparison.

In particular, FIG. 11 is a graph of measured leakage current for different capacitors with a 20-Å thick Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer having a larger thickness than the Al<sub>2</sub>O<sub>3</sub> dielectric layer. FIG. 12 is a graph of measured leakage current for different capacitors with a 25-Å thick Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer having a larger thickness than the Al<sub>2</sub>O<sub>3</sub> dielectric layer.

As is apparent from FIGS. 11 and 12, the leakage current characteristics are deteriorated when the thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is smaller than 1.

FIGS. 13 and 14 are graphs of leakage current versus thickness ratio of the  $Al_2O_3$  dielectric layer to the  $HfO_2$  dielectric layer, when the thickness ratio is larger than 1, for different capacitors with the composite  $Al_2O_3/HfO_2$  dielectric layer. In FIGS. 13 and 14, the leakage current characteristic of a capacitor with a single  $Al_2O_3$  dielectric layer is also shown for comparison.

In particular, FIG. 13 is a graph of measured leakage current for different capacitors with a 30-Å thick Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer having a thickness smaller than or equal to the Al<sub>2</sub>O<sub>3</sub> dielectric layer. FIG. 14 is a graph of measured leakage current for different capacitors with a 35-Å thick Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer having a smaller thickness than the Al<sub>2</sub>O<sub>3</sub> dielectric layer.

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As is apparent from FIGS. 13 and 14, the leakage current characteristics are favourable when the thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is greater than or equal to 1.

A capacitor of a semiconductor memory device according to the present invention has a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer, which is composed of an Al<sub>2</sub>O<sub>3</sub> dielectric layer and an HfO<sub>2</sub> dielectric layer, wherein a thickness ratio of the Al<sub>2</sub>O<sub>3</sub> dielectric layer to the HfO<sub>2</sub> dielectric layer is greater than or equal to 1. The leakage current characteristics of capacitors are improved with such a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer structure. In addition, when the Al<sub>2</sub>O<sub>3</sub> dielectric layer of the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer has a thickness of about 30-60Å, direct tunnelling through the dielectric layer of the capacitor is suppressed and stable leakage current characteristics are obtained. When the HfO<sub>2</sub> dielectric layer of the composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer has a thickness of about 40Å or less, crystallization of the HfO<sub>2</sub> dielectric layer and an accompanying increase in leakage current are suppressed.

With the capacitor according to the present invention that includes a composite Al<sub>2</sub>O<sub>3</sub>/HfO<sub>2</sub> dielectric layer with optimal thickness ratio between the two dielectric layers, the effect of suppressing increase in leakage current is maximized and superior electrical properties are obtained.

While this invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

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